Registry No. Captan, 133-06-2; ethanol, 64-17-5.

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A Gas Chromatographic Method for the Determination of Bendiocarb in Soil and Corn: Application to the Analysis of Residues in Corn

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Residues of bendiocarb were extracted from soil and corn by blending with ethyl acetate, purified by column chromatography with a 2:5 (w/w) mixture of Nuchar C charcoal and Whatman CF-11 cellulose, and analyzed by GLC-AFID with a glass column (75 cm × 2 mm i.d.) packed with 2% OV-101 on 80-100-mesh Ultra-Bond 20M. Recoveries ranged from 86.7 to 98.1%. Corn grown in a sandy silt loam soil treated with bendiocarb applied in the furrow with the seed at 1.7 and 2.5 kg of a.i./ha with or without Eradicane (EPTC plus antidote *N,N*-diallyldichloroacetamide) at 6.7 kg of a.i./ha contained bendiocarb residues of <0.05 ppm in various tissues. The average residue concentrations were significantly higher ($P = 0.05$) at the higher rate of bendiocarb soil treatment. There was no significant difference when bendiocarb was applied at the same rate with or without herbicide. The residue concentrations in various parts were in the order of kernels < cobs and husks < leaves plus stems. There was no significant difference in residues between cobs and husks.

Bendiocarb (2,3-isopropylidenedioxyphenyl methylcarbamate, Ficam) is a contact and stomach poison that is effective against a wide range of soil and structural pests (Spencer, 1982). Since its introduction by Agrochemical Division of Fisons, Ltd., in 1971, bendiocarb has been evaluated as a control agent against several agricultural pests in corn, sugar beet, and other crops (Lemon and McLeod, 1980; Bryan , 1980; Rimsa, 1980; Heijbroek, 1980; Mize et al., 1980). Little has been published on the residues of bendiocarb in crops resulting from soil applications of this chemical. The existing residue method for the determination of bendiocarb consists of solvent extraction, column chromatographic cleanup, alkaline hydrolysis of the parent compound, chemical derivatization of the resulting phenol, and then gas-liquid chromatographic analysis of the derivative (Whiteoak et al., 1978). This method is tedious and time consuming. Futhermore, in the preparation of the derivative with 2,4-dinitro-1-fluorobenzene, the pH, time, and temperature of the reaction are extremely critical.

Recently the direct GLC analysis of several carbamate insecticides has been reported (Lorah and Hemphill, 1974; Szeto and Sundaram, 1980), but neither cited reference specifically mentioned bendiocarb. This paper describes a simple and sensitive method for direct determination of bendiocarb in soil and in corn tissues. This method was used to determine the bendiocarb residues present in the parts of the corn when bendiocarb was applied in the furrow with the seed to control wireworms (*Agriotes obscurus* L). Eradicane (EPTC, *S*-ethyl dipropylcarbamothioate, plus antidote, *N,N*-diallyldichloroacetamide), generally used to control weeds in corn, was included in the experiment to determine if the combined bendiocarb–herbicide treatment would have any effect on the uptake of bendiocarb. The results are presented herein.

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EXPERIMENTAL SECTION

Apparatus. A Sorvall Omni-Mixer was used for the extraction of bendiocarb from corn tissues and soil. The GLC analyses were performed with a Tracor MT 222 gas chromatograph equipped with a Tracor Model 702-NP alkali flame ionization detector.

Reagents. Activated charcoal (Nuchar C, Kodak Laboratory Chemicals) was acid-washed prior to use (Brown, 1975), and a 2:5 (w/w) mixture of charcoal/Whatman CF-11 cellulose powder was prepared. Ethyl acetate and hexane were distilled in glass. Anhydrous Na_2SO_4 was heated overnight at 260 °C prior to use. An analytical standard of bendiocarb (>99%) was obtained from the Pesticides Standard Unit, Laboratory Service Division, Food Production and Inspection Branch, Agriculture Canada.

Sample Preparation and Fortification. Stock solutions (100, 10 and 1 μg/mL) of bendiocarb were prepared in ethyl acetate for sample fortification and appropriately diluted for use as the reference standard for GLC analyses.

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Table I. Percent Recovery of Bendiocarb from Various Corn Tissues and Soil after Fortification

substrate	% recovery ± SD (n = 4)		
	1.0 ppm	0.10 ppm	0.01 ppm
leaves plus stem	91.2 ± 1.6	89.5 ± 3.3	90.9 ± 8.9
husks	91.9 ± 1.4	92.1 ± 2.3	88.2 ± 10.8
kernels	92.9 ± 2.3	93.7 ± 2.1	86.7 ± 9.4
cobs	95.2 ± 2.1	95.4 ± 2.4	98.1 ± 6.7
soil	91.5 ± 0.8	92.6 ± 2.3	92.5 ± 2.4

Untreated silt loam (pH 5.76, 5.1% organic matter, 37.5% sand, 51.3% silt, and 6.1% clay) from the Substation, Agriculture Canada, at Abbotsford, British Columbia, was sieved to pass a 10-mesh screen. Aliquots of 50 g of air-dried soil with 9.8% residual moisture were weighed into 250-mL beakers and fortified separately at 1.0, 0.1, and 0.01 ppm with 0.5 mL of the appropriate stock solutions of bendiocarb. The solvent was evaporated at ambient temperature for about 2 h in a fume hood; the soil samples were mixed thoroughly during drying. When no trace of the solvent remained, they were stored at 4 °C for 24 h prior to extraction.

Corn collected from untreated plots was prepared by removing the kernels from the cobs and cutting the cobs, husks, and leaves plus stems into small pieces. Each separate sample was mixed thoroughly and stored at −18 °C in plastic bags. Similarly untreated corn tissues were fortified with bendiocarb separately to determine recovery. Fifty grams of the kernels and 20 g each of the cobs, husks, and leaves plus stems were treated with 1.0, 0.1, and 0.01 ppm of bendiocarb. They were allowed to stand at ambient temperature in a fume hood for about 2 h prior to extraction.

Sample Extraction. Prior to being blended, tissue samples were mixed with anhydrous Na_2SO_4; 20 g was used for the leaves plus stems, the husks, and the cobs, and 50 g was used for the kernels. Bendiocarb residues were extracted from the fortified corn tissue and soil samples by blending with 100 mL of ethyl acetate for 5 min. The Sorvall Omni-Mixer container was immersed in an ice–water bath while blending. The extracts from the corn tissue samples were filtered through a Büchner funnel lined with glass fiber filter paper. The filter cakes were extracted twice more with 50 mL of ethyl acetate, and all extracts were combined. The solvent from each blending of the soil samples was carefully decanted to retain the soil particles and the solvent was filtered through a Whatman No. 1 filter paper lining a sintered-glass funnel. The combined extracts were concentrated to about 2 mL in a flash evaporator at 35 °C and their final volumes adjusted to 10 mL for cleanup.

Cleanup. Glass columns (30 cm × 1.1 cm i.d.) with Teflon stopcocks were packed from bottom to top with a glass wool plug, 1.5 cm of anhydrous Na_2SO_4, 4 cm of a 2:5 (w/w) mixture of Nuchar-activated charcoal/Whatman CF-11 cellulose, 1.5 cm of anhydrous Na_2SO_4, and another glass wool plug. The packed columns were prewashed with 10 mL of ethyl acetate followed by 10 mL of hexane. Aliquots of crude extracts equivalent to 5 g of leaves plus stems, 10 g of husks, cobs, or kernels, or 25 g of soil were transferred quantitatively to the cleanup columns, and the resulting eluates were collected. Bendiocarb was eluted with 20 mL of 40% ethyl acetate in hexane. Cleaned extracts were concentrated in a flash evaporator at 35 °C for GLC analysis.

GLC Analysis. A glass column (75 cm × 2 mm i.d.) packed with 2% OV-101 on 80–100-mesh Ultra-Bond 20M (Ultra Scientific) was used. Helium was the carrier gas at 60 mL/min. The operating parameters were as follows: detector temperature 240 °C; inlet and outlet temperature 210 °C; column temperature 165 °C; plasma gas flow rate 3.5 mL/min for hydrogen and 120 mL/min for air.

Detector response was calibrated daily with analytical standards. Quantification was based on average peak heights of these external standards, which were injected before and after the sample.

Field Study. A field trial to determine bendiocarb residues in various parts of sweet corn (cv. Jubilee) after soil application of this chemical was conducted in a sandy silt loam at Agassiz, British Columbia. Eradicane was applied to half the plots as a spray at 6.7 kg of a.i./ha and rotovated into the soil. Each plot was a single 15 m long row with 2.4 m between rows. Sixteen seeds, equally spaced, were planted in each plot. The bendiocarb granules were placed in the furrow with the seed at 1.7 and 2.5 kg of a.i./ha. Each treatment was replicated 4 times. The treatments were made and the corn was planted on June 2, 1982, and the corn was harvested on Sept 21, 1982. Four treatments were evaluated: bendiocarb alone at 1.7 and 2.5 kg of a.i./ha and Eradicane plus bendiocarb at 1.7 and 2.5 kg of a.i./ha. Four mature corn plants were collected from each plot, and an equal amount of the leaves plus stems, husks, cobs, and kernels were removed separately from each plant, cut up, and thoroughly mixed in plastic bags to form composite samples. The samples were stored at −18 °C until they were analyzed. Bendiocarb residues were determined as described in the previous section. The four replicates of each treatment were analyzed separately.

RESULTS AND DISCUSSION

Recoveries of Residues from Corn Tissues and Soil. The cleanup achieved by the Nuchar-activated carbon/Whatman CF-11 cellulose column was excellent. Cleaned extracts of unfortified controls equivalent to 5 g of leaves plus stems, 10 g each of husks, cobs, or kernels, or 25 g of soil contained no GLC response that interfered with bendiocarb. Under the GLC conditions described, the abolute retention time of bendiocarb was 1.25 min. Bendiocarb appeared to be stable on the GLC column; no column

Table II. Bendiocarb Residues in Corn Grown in a Sandy Silt Loam Treated with Bendiocarb and Eradicane

treatment	residues, ppm ($\bar{X}$ ± SE, n = 4), and range, ppm[a]			
	leaves plus stems	husks	cobs	kernels
bendiocarb at 1.7 kg of a.i./ha	0.012 ± 0.004	0.005 ± 0.002	0.004 ± 0.001	0.003 ± 0.002
	0.005-0.020	ND[b]-0.010	ND-0.005	ND-0.007
bendiocarb at 1.7 kg of a.i./ha plus Eradicane	0.012 ± 0.005	0.007 ± 0.003	0.005 ± 0.003	ND
	ND-0.021	ND-0.011	ND-0.014	ND
bendiocarb at 2.5 kg of a.i./ha	0.024 ± 0.006	0.018 ± 0.005	0.011 ± 0.003	0.001 ± 0.001
	0.011-0.038	0.005-0.026	0.003-0.016	ND-0.005
bendiocarb at 2.5 kg of a.i./ha plus Eradicane	0.023 ± 0.007	0.018 ± 0.007	0.016 ± 0.005	0.001 ± 0.001
	0.010-0.043	0.007-0.036	0.008-0.027	ND-0.005

[a] Residues are listed first and the range is the second number. [b] ND = not detectable at the limit of detection of 0.002 ppm.

priming was necessary to obtain a stable response, and similar responses were obtained with the reference standards prepared in pure ethyl acetate or in cleaned sample extracts.

The extraction efficiency of the described method for weathered field samples was evaluated. Aliquots of corn tissues collected from plots treated with bendiocarb at 2.5 kg of a.i./ha were extracted separately by the following methods: (1) blending with ethyl acetate as described herein, (2) refluxing with hydrochloric acid (Cook et al., 1969; Robinson, 1982), and (3) refluxing with dichloromethane (Whiteoak et al., 1978). Bendiocarb residues detected by methods 2 and 3 were about 60% of those detected by method 1, indicating that the described method is more effective for extracting bendiocarb from weathered field samples than previous proposed methods. Moreover the ethyl acetate extracts contained less coextractives than the acid extracts.

The Abbotsford silt loam was chosen for recovery study because it is similar to the sandy silt loam in the experimental plots at Agassiz. Percentage recoveries for fortified corn tissues and soil are presented in Table I. Each mean percentage with its standard deviation was derived from four replicates. The mean recoveries of bendiocarb ranged from 86.7 to 98.1% for both corn tissues and soil. Since 0.3 ng of bendiocarb gives about 30% full-scale delfection at 10 × 1 attenuation and the cleaned extracts can be concentrated to 0.5 mL for GLC analysis, the limit of detection of the described method may well be below 0.01 ppm for corn tissues and soil.

Residues in Corn Tissues. Bendiocarb residues detected in various corn tissues are given in Table II. Only small amounts of residues (<0.05 ppm) were found; thus, very little bendiocarb was accumulated in corn after soil treatment with this chemical. The residue concentration in leaves plus stems, husks, and cobs correlated with the rate of soil treatment with bendiocarb. After soil application of bendiocarb at the higher rate, i.e., 2.5 kg of a.i./ha, significantly higher concentrations of residue were found in those tissues ($P = 0.05$). However, there was no significant difference in residues accumulated in kernels after soil application of bendiocarb at 1.7 or 2.5 kg of a.i./ha. The addition of Eradicane in the soil treatments appeared to have no significant effect on the accumulation of bendiocarb in various corn tissues ($P = 0.05$). When soil treatments with bendiocarb were at the same rate, there was no difference in residues in various corn tissues whether or not the herbicide, Eradicane, was included in the soil treatments. Taking into consideration all four treatments of soil in this study, there was a significant difference in residue concentrations in various corn tissues ($P = 0.05$). They were in the order of kernels < cobs and husks < leaves plus stems. There was no significant difference between cobs and husks.

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Leaf, Fruit, and Soil Surface Residues of Carbosulfan and Its Metabolites in Florida Citrus Groves

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Carbosulfan was applied to a Florida orange grove in the fall of 1981 and again 3 months later at one-fourth the fall rate. Dissipation was rapid from fruit and leaf surfaces in each experiment but was significantly more rapid during the fall than in winter. Persistence of carbosulfan along the soil dripline exceeded that on fruit or leaf surfaces in each experiment. Very little carbosulfan was detected midway between trees. The major observed metabolite of carbosulfan was carbofuran. In each experiment, carbofuran was more persistent on leaf surfaces than the parent compound. Safe worker reentry intervals, estimated from toxicity studies on rats, were determined to be 3 days for the fall application rate of 4 lb of a.i./acre and 1–2 days for the winter rate of 1 lb of a.i./acre.

Carbosulfan (CS) [2,3-dihydro-2,2-dimethyl-7-benzofuranyl [(di-*n*-butylamino)thio]methylcarbamate] is a derivative of carbofuran (CF) and a candidate broad-spectrum pesticide for Florida citrus. Degradation of CS has been studied in soil (Clay et al., 1980) and plants (Umetsu et al., 1979). Principal metabolites reported were CF, 3-hydroxycarbofuran, and 3-ketocarbofuran. CS has an oral LD_{50} of 209 mg/kg (rat) vs. 11 mg/kg (rat) for CF ("Farm Chemicals Handbook", 1982). The safe reentry of harvesters into pesticide-treated fields requires an understanding of the environmental behavior of toxic compounds and their metabolites. This study was undertaken

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